# ADSORPTION OF AQUEOUS COPPER ON PEANUT HULLS

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By

Kanika Octavia Davis

Director: Dr. Carmen L. Huffman
Associate Professor of Chemistry
Chemistry and Physics Department

Committee Members:
Dr. Scott W. Huffman, Chemistry
Dr. David D. Evanoff, Chemistry

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| Abbreviation/Symbol | Definition |
|---|---|
| $q_e$ | surface coverage at equilibrium (mg $Cu^{2+}$/g hull) |
| $q$ | surface coverage (mg $Cu^{2+}$/g hull) |
| $C_e$ | concentration of aqueous copper at equilibrium (ppm) |
| $C_o$ | concentration of aqueous copper (ppm) |
| $Q_o$ | Langmuir maximum surface coverage (mg $Cu^{2+}$/g hull) |
| $b$ | Langmuir binding constant (L/mg) |
| $R_L$ | adsorption intensity |
| $\Delta G_{ads}$ | free energy of adsorption (kJ/mol) |
| $R$ | gas constant (8.314 J/mol K) |
| $T$ | temperature (K) |
| $K_R$ | Redlich-Peterson constant (L/g) |
| $a_R$ | Redlich-Peterson constant (Lm/g) |
| β | Redlich-Peterson constant |
| $t$ | time (min) |
| $k_1$ | pseudo-first order rate constant ($min^{-1}$) |
| $k_2$ | pseudo-second order rate constant (g hull/mg $Cu^{2+}$ min) |
| FT-IR | Fourier transform infrared |
| SEM | scanning electron microscopy |
| EDX | energy dispersive x-ray |
| ICP-OES | inductively coupled plasma optical emission spectroscopy |
| $D$ | exponential association parameter (mg $Cu^{2+}$/g hull) |
| $B$ | exponential association fitting parameter ($min^{-1}$) |
| $A$ | absorbance |
| $l$ | path length (μm) |
| $c$ | concentration of $COO^-$ sampled by the spectrometer (M) |

# ABSTRACT

ADSORPTION OF AQUEOUS COPPER ON PEANUT HULLS

Kanika Octavia Davis

Western Carolina University (March 2014)

Director: Dr. Carmen L. Huffman

A method was established for measuring the adsorption of Cu(II) from aqueous solution to unmodified and modified peanut hulls at constant temperature and pH. Modification of the hulls was performed by oxidation with alkaline hydrogen peroxide. During the modification process, the hydrogen peroxide solubilizes the lignin component, making the surface more porous which increases the availability of binding sites, while simultaneously oxidizing the cellulose. The oxidation of alcohol groups creates more binding sites by creating functional groups such as $COO^-$, which increases chelation to metal ions. Fourier transform infrared spectroscopy confirms delignification of the peanut hulls by the disappearance of carboxyl peaks of the modified hulls, which were originally produced from the lignin content. Although, oxidation is not fully confirmed, it is not ruled out because the expected carboxylate peak (1680 $cm^{-1}$) maybe overshadowed by a broad peak due to OH bending of water adsorbed to the hulls.

Hulls adsorbed copper from solutions in the concentration range of 50-1000 ppm of $CuCl_2$. Concentrations of pre- and post-adsorption solutions were determined using inductively coupled plasma optical emission spectroscopy. The adsorption isotherms were fit to known two and three-parameter models, evaluated and the binding mechanism was inferred. Maximum surface coverage was 3.5 ± 0.6 mg $Cu^{2+}$/g hull for unmodified

hulls and 11 ± 1 mg $Cu^{2+}$/g hull for modified hulls. The adsorption for the hulls is best described by the Langmuir model, suggesting monolayer, homogeneous adsorption. With a free energy of adsorption of 10.5 ± 0.9 kJ/mol for unmodified hulls and 14.5 ±0.4 kJ/mol for modified hulls, the process is categorized as chemisorption for both types of hulls. The adsorption for both hulls is also described by the Redlich-Peterson model, giving β nearer to 1 than 0, which further suggests homogeneous adsorption described by the Langmuir model. After rinsing the hulls, scanning electron microscopy images coupled with energy dispersive X-ray spectroscopy showed that the percentage of copper on the modified hulls (2.5 %) was greater than on the unmodified hulls (1.6 %). This study concluded that the adsorption of copper using peanut hulls is a potential method for wastewater treatment and delignification and oxidation of the hulls increases the adsorption capacity approximately three-fold.

# CHAPTER 1: INTRODUCTION

## MOTIVATION

The release of heavy metals or toxic metals, such as copper, lead, zinc, and cadmium, into the environment is a great concern throughout the world because these metals have negative effects on the environment and the health of humans and animals. For example, China is constantly suffering from heavy metal pollution. According to the Institute of Public and Environmental Affairs, the amount of grain in China polluted by heavy metals was estimated to have reached 12 million tons per year in 2006. A result was an economic loss of more than 20 billion yuan, about 3.25 billion dollars. China's heavy metal pollution problem threatens their ecological environment, food security, the development of agriculture, and public health since heavy metals are toxic and some are considered carcinogenic.[1] There are other countries in Africa and the Middle East with similar problems. Heavy metals are making their way into aqueous environments and are among the top water pollutants today. More importantly, with the growth of industrialization such as mines, metal plating, tanneries, pesticides, paint manufacturing, and many more, the concentrations of these metals in water are increasing.[2,3] Unlike some other pollutants, heavy metals are non-biodegradable, can build up to toxic concentrations, and have a harmful effect on the environment.

Copper is a common pollutant among these toxic metals that is widely used in many industries, having numerous opportunities to make its way into wastewater and natural waters. The manufacturing of electrical wiring, pipes for plumbing, and air conditioning tubing is one way industries are releasing copper into wastewater, but the main sources are from copper mines and road runoff, where brakes and engine parts from

automobiles release copper onto the road.[4] Some copper (0.9 mg in human adults) is essential for living organisms, but excessive amounts can be extremely detrimental to human health.[5] The Agency for Toxic Substances and Disease Registry states that exposure to copper can irritate the nose, mouth, and eyes. It can cause headaches, dizziness, nausea, diarrhea, abdominal pain from ulcers, liver and kidney damage, brain and blood disorders, and even death.[6] Due to the many health concerns and the need to protect the environment, removal of copper from effluents is vital and now legally imposed by the United States Environmental Protection Agency and other environmental organizations around the world.[7]

Wastewater treatment plants use several methods for the removal of heavy metals including chemical precipitation, coagulation, floatation, ion exchange, reverse osmosis, electrodialysis, and electrolysis.[3] Some of these methods have major disadvantages, such as the large volumes of sludge produced in precipitation methods. There are extra treatments needed to handle the disposal of the sludge which can become inconvenient and time consuming.[8] Ion exchange methods require a high capital investment and large operational costs because the equipment is quite complex and sophisticated. Parts are subject to breaking down and closer operator attention is required which comes with a higher cost. Also, resins (polymers that allow the trapping and releasing of ions to occur) can become fouled with contaminants and degrade over time which hinders the exchange process.[9] Electrodialysis and reverse osmosis are processes involving the transfer of ions across membranes. Membranes are unstable in various wastewater conditions. The precipitation of inorganic salts and particulates of metal oxides in the water and the growth of microbiological organisms on the membrane's surface can cause membrane

fouling. This degree of instability requires frequent membrane replacement and pretreatment.[9] Electrolysis uses a direct current through the wastewater to separate and remove ionic species. It is inefficient at low metal concentrations because it is harder for the electrodes to differentiate between the reactivity of different ions in solution. Therefore, there is a need for a more efficient method that is highly selective, easy to operate, and cost effective.

Adsorption, defined as the attachment of particles to a surface, is an effective method for removing heavy metals from aqueous solutions. When an adsorbent is placed into an aqueous solution containing contaminants such as heavy metals, the metal ions adhere to its surface, thereby decreasing the metal concentration in solution. The study outlined here focuses on the removal of copper using biosorption, a special case of adsorption where the adsorbent is biodegradable. Biosorption is a simple technique: the adsorbent is mixed with the contaminated solution, the contaminant adheres to the surface of the adsorbent, and the adsorbent along with the adsorbed contaminant is then removed by filtering. Since the adsorbent is biodegradable, the solid waste decomposes, which makes the waste more compact, easier to handle, and available for use in bio-energy processes. Some adsorbents have good adsorption capacities and have highly selective adsorption of heavy metal ions. The process is efficient at low concentrations and inexpensive since the adsorbents are readily available and easy to regenerate. Some agricultural by-products that have shown positive results for adsorption of metals are wood, leaves, sawdust, peanut hulls, orange peels, wheat bran, and rice husks.[2] The by-product of interest in this study is peanut hulls. The goal is to examine the adsorption of copper by unmodified and modified peanut hulls in order to determine the binding

mechanism. There are a few studies about adsorption of heavy metals using peanut hulls, but little is known about the binding mechanism.[2,4,10]

## PEANUT HULLS

Over four billion pounds of peanuts are produced annually in the United States. Since peanuts are grown as a plant, they are a renewable resource.[11] As a by-product, the hulls are easy and inexpensive to obtain because industries are in need of only the peanut as the main ingredient in their products.

Peanut hulls are very porous and have low solubility. The majority of their chemical composition is fiber (60-67%) including cellulose and lignin. The composition of peanut hulls is shown in

Table 1.[12] The total analysis does not summate to 100% because the fiber includes much of the cellulose and lignin. Agricultural by-products showing high adsorption capacities for metals tend to contain cellulose, hemicellulose, pectin, lignin, and protein.[13] Peanut hulls have similar components, making them a good candidate for use in wastewater treatment. The structures of these compounds have functional groups that invite metal ion exchange and metal chelation. The structure of cellulose is shown in Figure 1. Cellulose is a polymer of glucose units, which are composed of primary and secondary alcohols, joined by ester linkages. The structure of lignin is shown in Figure 2. Lignin is a complex polymer composed of individual aromatic units. The structure is not known precisely because of lignin's complexity. There are many binding possibilities between the three phenyl propane monomers of which lignin is composed.[14]

*Table 1. Characteristics of peanut hulls.*[11,12]

| | | |
|---|---|---|
| Chemical Characteristics | Moisture | 8-10 % |
| | Protein | 6-7 % |
| | Fat | 1% |
| | Fiber | 60-67 % |
| | Cellulose | 35-45 % |
| | Lignin | 27-33 % |
| | Ash[a] | 2-4 % |
| Physical Characteristics | Porosity | 61.7 % |
| | Solubility in $H_2O$ | 0.74 % |
| | Bulk density | 5-7 lb/ft$^3$ |

[a] Contributed by soil adhering to peanut hull during analysis.

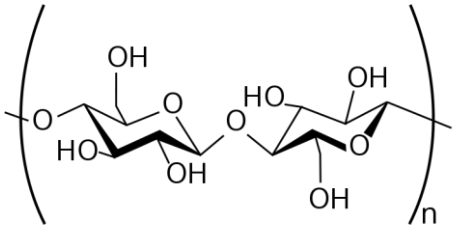


*Figure 1. Structure of cellulose.*[15]

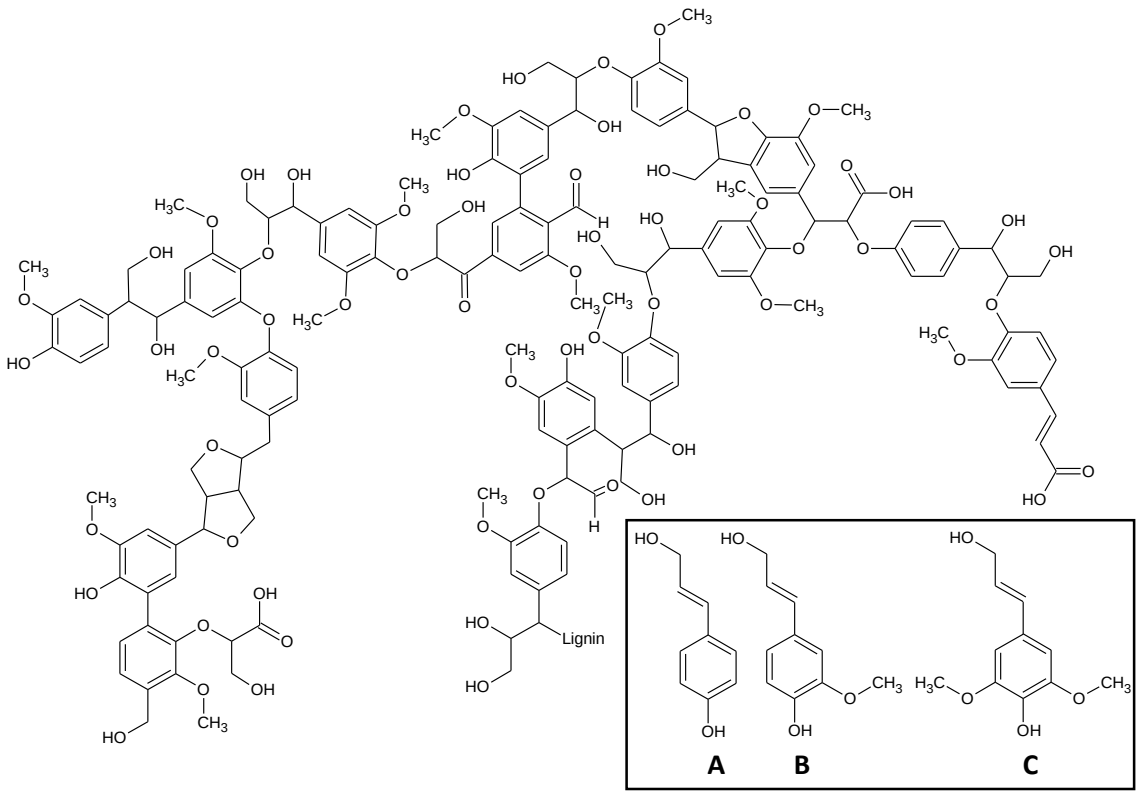


*Figure 2. Structure of lignin with its three phenyl propane monomer precursors (inset): A) p-coumaryl alcohol, B) coniferyl alcohol, and C) sinapyl alcohol.*[16]

Chemical modification of the hulls will help determine the type of binding involved in the adsorption process. Differences in adsorption among different treatments may indicate the chemical nature of the binding interaction. The pretreatment to be performed in this study is the alkaline oxidation/delignification of the hulls. The biopolymers contain a variety of functional groups, such as alcohol groups, which can be chemically altered to possibly enhance the adsorption of metal ions. Oxidation of the hulls involves oxidizing the alcohol groups of the cellulose into carboxylate groups, which would create a cationic exchanger for the metal ions, increasing adsorption.[17] The newly formed carboxylate groups exchange cations, meaning the counterion (Na in this case) leaves the carboxylate group and the metal ion in solution attaches in its place as shown in the reaction scheme below.[17–19]

$$2\ RCOONa + Cu^{2+} \rightarrow (RCOO)_2Cu + 2\ Na^{+} \quad (1)$$

This modification has been tested in previous studies on adsorbents composed of mainly cellulose and lignin, such as jute fibers, resulting in enhanced effectiveness of metal ion adsorption.[2,17] Peanut hulls have a similar composition to these adsorbents, as described in

Table *1*. Therefore, a similar increase in adsorption capacity is expected.

Delignification is the removal of lignin from the peanut hulls. This occurs in the alkaline oxidation process due to the solubility of lignin in the oxidizing solution. Without the bulky structure of lignin present in the hulls, the hulls are more porous, and the copper ions would be able to access more of the cellulose binding functional groups.[18,20,21] In the current study, an adsorption capacity for unmodified hulls was established and the modification discussed was carried out on the hulls to determine whether the process increases adsorption.

## ADSORPTION ISOTHERMS

Adsorption isotherms are models used to characterize the relationship between the adsorbate (solute) and the adsorbent (solid). In this case, the adsorption isotherm would describe how the copper ions are interacting with the peanut hull material. Several two- and three-parameter isotherms were used in the analysis, but only the two that best fit the data are defined here.

The Langmuir model is a two-parameter isotherm describing homogenous, monolayer adsorption with a set number of identical binding sites and no interaction between the adsorbed molecules. The Langmuir equation is given below[22]

$$q_e = \frac{Q_o b C_e}{1 + b C_e} \tag{2}$$

where $q_e$ is surface coverage at equilibrium (mg $Cu^{2+}$/g hull), $Q_o$ is the maximum coverage capacity (mg $Cu^{2+}$/g hull), $b$ is an equilibrium constant (related to free energy of

adsorption (L/mg $Cu^{2+}$)), and $C_e$ is the solution concentration at equilibrium. Parameters can be determined by using the linearized equation:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC_e} \quad (3)$$

where $1/q_e$ is plotted as a function of $1/C_e$. Adsorption intensity ($R_L$) is defined as

$$R_L = \frac{1}{1 + bC_o} \quad (4)$$

where $C_o$ is the initial concentration in solution (mg/L). If $R_L$ falls between 0 and 1, then adsorption is favorable. If $R_L = 1$, then $b$ would be very low, indicating adsorption is linear (independent of $C_o$). If $R_L = 0$, $b$ would be very large, indicating the adsorption is irreversible (i.e. binding is so strong that the adsorbate cannot be removed). If $R_L > 1$, adsorption is unfavorable.[4]

Gibbs free energy of adsorptoin ($\Delta G_{ads}$) is used to classify the binding mechanism as physisorption or chemisorption. The larger the $\Delta G_{ads}$, the more likely the binding is chemisorption. Some authors have used 8 kJ/mol as a cut-off value for physisorption vs. chemisorption.[4] $\Delta G_{ads}$ can be computed using $b$ from the Langmuir equation as shown below:

$$\Delta G_{ads} = -RT \ln b \quad (5)$$

where $R$ is the gas constant (8.314 J/K mol) and $T$ is temperature (K).[23,24]

The Langmuir model is a common model used in biosorption studies. Another common model is the Freundlich model, which is a two-parameter model like the

Langmuir model, except it describes heterogeneous adsorption. Adsorption here is multilayered, and there is not an equal affinity for binding sites.

The Redlich-Peterson model is a three-parameter isotherm, combining the Langmuir and Freundlich equations to describe homogeneous and heterogeneous adsorption over a wide concentration range.[22] The Redlich-Peterson equation is:

$$q_{\mathrm{e}} = \frac{K_{\mathrm{R}} C_{\mathrm{e}}}{1 + a_{\mathrm{R}} C_{\mathrm{e}}^{\beta}} \tag{6}$$

where $K_{\mathrm{R}}$ (L/g), $a_{\mathrm{R}}$ (L/mg), and β are Redlich-Peterson isotherm constants.[25] Behavior of adsorption is summarized by β, which lies between 0 and 1. As β approaches 0, the adsorption is characterized by the Freundlich model and as β approaches 1, the adsorption is characterized by the Langmuir model.[25] Parameters can be determined by using software to fit data to the linearized equation:

$$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = \beta \ln C_e + \ln a_R \tag{7}$$

where $\ln(K_R (C_e/q_e)\text{-}1)$ is plotted as a function of $\ln C_e$.

## ADSORPTION KINETICS

Kinetics studies are used to determine when the hulls in copper solution reach equilibrium. The one phase exponential association function was used to fit a kinetics plot of $q_e$ vs. $t$ and to determine the maximum surface coverage:

$$q_e = D(1 - e^{-Bt}) \tag{8}$$

where $D$ and $B$ are fitting parameters. $B$ is greater than 0, and $D$ is the value of $q_e$ at the horizontal asymptote and therefore represents maximum surface coverage (mg $Cu^{2+}$/g hull).[26]

Kinetic models to describe the mechanism for biosorption are pseudo-first order and pseudo-second order kinetic models. The rate constants derived from the pseudo-first and pseudo-second order models are based on the following reaction:

$$Cu^{2+}(aq) + site \rightarrow Cu^{2+}(ads) \quad (9)$$

where $Cu^{2+}(aq)$ is the copper free in solution, the site is the binding sites available for adsorption, and $Cu^{2+}(ads)$ is the copper bound to the site.

In second order kinetics, the rate would be as follows:

$$Rate = k[Cu^{2+}(aq)][sites] \quad (10)$$

but since the $[Cu^{2+}(aq)]$ is in large excess, it is approximately constant throughout the adsorption process and the reaction only depends on [sites]. Therefore, by setting $k[Cu^{2+}(aq)] = k_1$, the rate becomes pseudo-first order as show below:[27]

$$Rate = k_1[sites] \quad (11)$$

Pseudo-second order kinetics follows the same principle as the pseudo-first order kinetic model, except the rate is

$$Rate = k[Cu^{2+}(aq)][sites]^2 \quad (12)$$

and would become pseudo-second order by setting $k[Cu^{2+}(aq)] = k_2$ as shown below:[27]

$$Rate = k_2[sites]^2 \quad (13)$$

The rate constant for adsorption can be calculated using the Lagergren equation:

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (14)$$

where $q$ (mg $Cu^{2+}$/g hull) is surface coverage at a given time ($t$) and $k_1$ ($min^{-1}$) is the pseudo-first order rate constant.[4,27] The value of $k_1$ can be calculated from the slope of the plot of $\ln(q_e - q)$ versus $t$. Equation 15 is a linearized equation for a pseudo-second order kinetic model:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (15)$$

where $k_2$ (g hull/(mg $Cu^{2+}$ min)) is the pseudo-second order rate constant, which can be calculated from the y-intercept of a plot of $t/q$ versus $t$. ($q_e$ can be calculated from the slope.)[4,27]

# CHAPTER 2: METHODS

## PEANUT HULLS

The peanuts in shell (roasted and unsalted) were purchased from Ingles located in Sylva, North Carolina, USA. The hulls were separated from the peanuts and the seed coats by hand, then ground with a coffee grinder and sieved using USA test standard stainless steel sieves of mesh sizes between 0.038 mm and 2.00 mm. All experiments were performed using hulls sized between 0.50 and 1.00 mm. The hulls were rinsed with hot and cold ultrapure water from a Milli-Q water filtration system purchased from Millipore (Billerica, MA, USA) and dried in a drying oven (VWR International, Radnor, PA,USA) at 60°C overnight.

## CHEMICALS

Copper solutions were prepared in plastic containers using laboratory grade copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, Fisher Scientific, Waltham, MA, USA) and ultrapure water. A pH of 4 was maintained by utilizing a buffer solution prepared with a pHydrion buffer capsule (Micro Essential Laboratory, Brooklyn, NY, USA; contents: potassium biphthalate) since previous studies have shown acidic solutions provide the optimum condition for adsorption.[4,10] Dilutions for the analysis were made using trace metal grade nitric acid (5% solution) and the oxidative treatment used hydrogen peroxide (certified ACS 30%) and sodium hydroxide, all acquired from Fisher Scientific. Microcrystalline cellulose from Acros Organics (Geel, Belgium; particle size of 50 μm) and commercial alkali lignin from Tokyo Chemical Industry Co. (Chuo-ku, Tokyo, Japan) were used for adsorption comparison.

## PARTICLE SIZE ANALYSIS

The size distribution of the peanut hull particles from the 0.50-1.00 mm sieve was determined by a particle size analyzer (Mastersizer 2000 with Hydro 2000G by Malvern Instruments, Malvern, UK). The blue light source is at a wavelength of 470 nm, and the red light source is at a wavelength of 633 nm. The bath was stirred at a rate of 1000 rpm and the pump ran at 1250 rpm. The dispersant was water and the particle absorption index was set to 0.1. For analysis, the refractive index of sawdust (1.53) was chosen since both it and the hulls are composed predominantly of cellulose and lignin. The process was completed 10 times and the data was averaged.

## HULL MODIFICATION

Oxidized substrates (hulls and cellulose) were prepared by adding them to a solution containing 30% hydrogen peroxide and 0.94 M - 0.97 M sodium hydroxide. The solution was slowly heated to 80 °C for 4 to 6 hours, filtered, rinsed subsequently with hot and cold water and left to dry in an oven over night at 60 °C. Chemical analysis of the product was conducted using Fourier transform infrared spectroscopy (FT-IR) (SpectrumOne with Universal ATR Sampling Accessory by PerkinElmer Instruments, Waltham, MA, USA). The spectral range was 650 - 4000 $cm^{-1}$ with a resolution of 4 $cm^{-1}$. Sixteen scans were acquired for each sample. Samples were measured several times. The data was then normalized at a common wavenumber and averaged. The modified and unmodified peanut hull IR spectra were normalized to a peak at 1026 $cm^{-1}$. The modified and unmodified cellulose IR spectra were normalized to a peak at 664 $cm^{-1}$.

## ADSORPTION

Solutions of copper (II) chloride ranging from 50 ppm to 1000 ppm by mass were prepared using Milli-Q water. About 0.5 g of the substrate (peanut hulls or cellulose) were placed in 15 mL plastic conical vials with about 10 g of copper (II) chloride solution. The solutions were rotated at 8 rpm using a shaker rotisserie (Thermo Scientific) for 24 hours at an average temperature of 21.0 – 23.7 °C. (Studies show that adsorption increases slightly with an increase in temperature.[4] In this study, room temperature was chosen for convenience.) After mixing, the samples were filtered using syringe filters (Whatman Schleicher & Schuell, Piscataway, NJ, USA; 13 mm diameter and 0.45 μm pore size) and diluted with 5% nitric acid for metal concentration analysis. Using the method of standard addition to account for possible matrix effects,[23] the concentration of $Cu^{2+}$ in the aqueous solution before and after adsorption was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Optima 4100 DV from PerkinElmer Instruments, Waltham, MA, USA). The ICP-OES utilized a pump flow rate of 1.5 mL/min, gas flows of plasma at 15 L/min, the auxiliary at 0.2 L/min, and the nebulizer at 0.80 L/min. The peak wavelengths observed for copper emission were 327, 325, 225, and 214 nm.

## KINETICS

The kinetics of $Cu^{2+}$ adsorption to the peanut hulls was studied by monitoring the adsorption process with a 1000 ppm copper (II) chloride solution over a 12 hour period. A portion of the sample was removed from the vial every hour. The portions were filtered, diluted, and the method of standard addition was used with ICP-OES to determine the concentration of $Cu^{2+}$ before and after adsorption.

## MICROSCOPY

The peanut hulls were examined using a compound light microscope (Leica DME, Wetzlar, Germany) and a scanning electron microscope (SEM, Hitachi S-3400N; Tokyo, Japan). SEM microscopy was performed at the Electron Microscope Laboratory located at the Clemson University Advanced Materials Center (Anderson, SC, USA). Modified and unmodified peanut hulls (both with and without copper) were mounted on the sample stage using carbon tape. Using the variable pressure mode, samples were maintained at 30 Pa. A voltage of 20 kV was applied, and backscatter electrons were detected to form the image. Concentration maps of oxygen, carbon, and copper on the hull surface were produced by energy dispersive x-ray (EDX) spectroscopy (Oxford Instruments X-Max$^{N}$, length 0.305 m; Abingdon, Oxfordshire, England) and displayed using the map feature in the software (AZtecEnergy by Oxford Instruments).

# CHAPTER 3: RESULTS AND DISCUSSION

## PEANUT HULL PARTICLE SIZE

The ground hull particles are of various shapes and textures. Images of the ground peanut hulls were taken using a compound light microscope (Figure 3). The pieces are both thick and thin. Some are flat and some are rod shaped. There are also pieces that are ridged around the edges. A particle size analysis was conducted to determine size distribution and an average particle size (Figure 4). The majority of the hulls (~60 %) are between 0.84 mm and 1.5 mm with an average size of 1.33 ± 0.04 mm, the uncertainty being the square of the standard error from fitting the data to a normal distribution. The particle size analyzer cannot measure particles greater than 2 mm, therefore the size distribution of hulls above 2 mm is unknown. The previous adsorption studies from which the results will be compared used hulls that were 0.710-1.000 mm.[3]

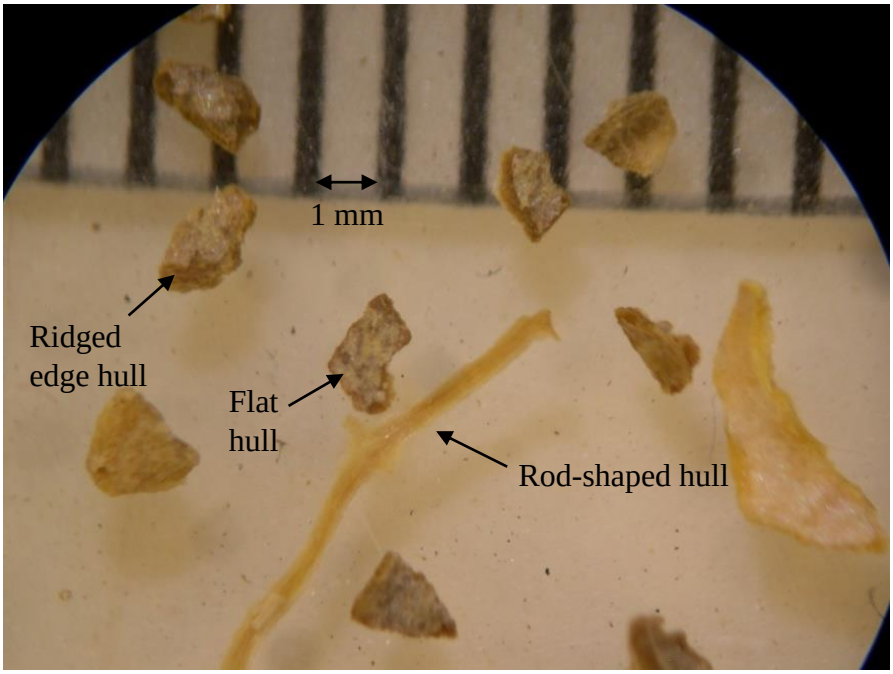


*Figure 3. Compound light microscope image of hull pieces on a mm scale.*

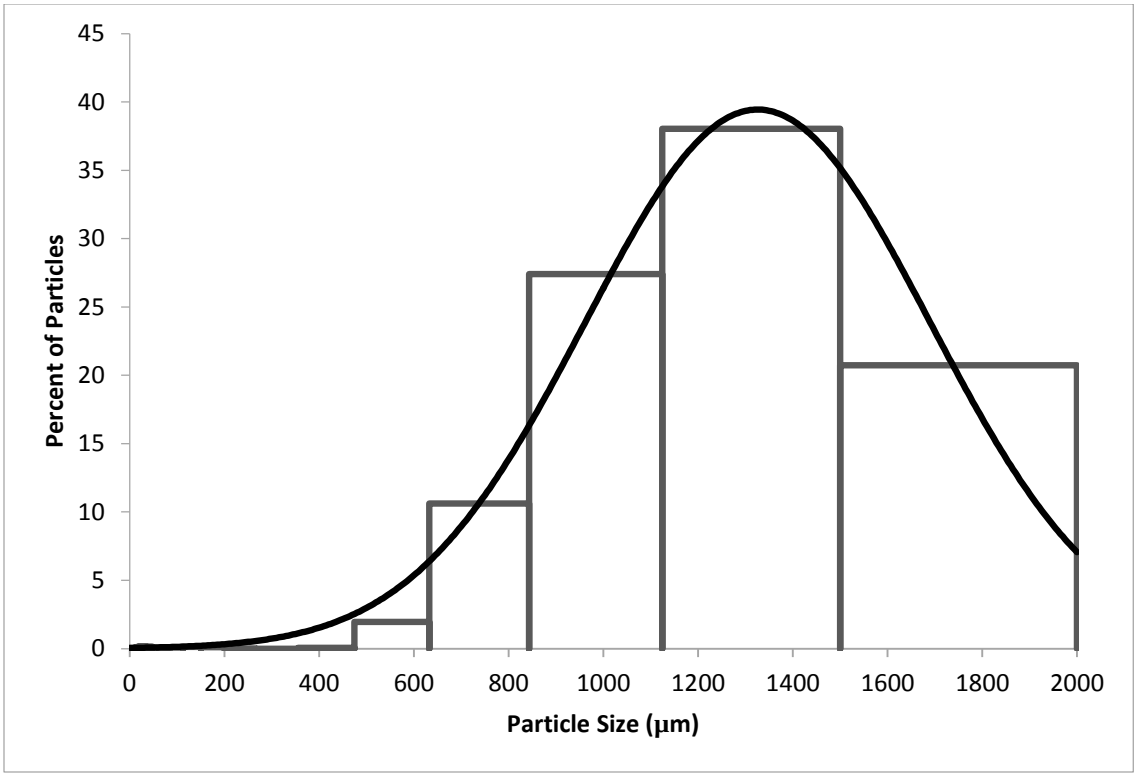


*Figure 4. Particle size distribution for the hulls used in adsorption experiments. The solid line is a normal distribution fit to the data.*

ADSORPTION KINETICS

The rate of copper adsorption by unmodified peanut hulls was examined by monitoring surface coverage ($q_e$) from a Cu(II) solution with an initial concentration of 1000 ppm at room temperature over time. Results are shown graphically in Figure 5. Coverage increases rapidly in the first 250 minutes, then increases gradually as the system approaches equilibrium. The maximum surface coverage, *D*, given by the fit to Equation 8 is 2.99 ± 0.09 mg $Cu^{2+}$/g hull, which is slightly lower than the maximum surface coverage (3.5 ± 0.6 mg $Cu^{2+}$/g hull) measured for the unmodified hulls equilibrating with a 1000 ppm solution for 24 hours in an adsorption experiment. The difference likely exists because the kinetic experiment ran for 12.5 hours, while the adsorption process was 24 hours. If the experiment was performed for a longer time, one

can presume that the additional data points at great *t* would cause the fit to level off at around 3.5 mg $Cu^{2+}$/g hull since some data points at $t > 600$ min have this value for $q_e$. The data suggest that equilibration time is approximately 12 hours. For typical adsorption experiments, hulls were in solution for at least 24 hours, which is well beyond the required equilibration time.

The data was modeled using the Lagergren pseudo-first order model and a pseudo-second order model.[27] The rate constants, correlation coefficients, and the theoretical adsorption capacity was calculated for the two models according to Equations 14 and 15 and are summarized in Table 2. Figure 6 shows the pseudo-first order kinetic model, a plot of $\ln(q_e-q)$ versus *t*. The theoretical adsorption capacity determined by pseudo-first order kinetics is lower than the experimental value ($3.4 \pm 0.4$ mg $Cu^{2+}$/g hull) and the correlation coefficient was low. However, a plot of $t/q$ versus *t* showed very good linearity indicating that the adsorption follows a pseudo-second order mechanism (Figure 7). The theoretical adsorption capacity determined by pseudo-second order kinetics differs from the experimental values by only 2 %, and the correlation coefficient is 0.9745. A pseudo-second order adsorption mechanism assumes the rate of occupying adsorption sites is proportional to the square of the number of unoccupied sites.[4] These results confirm the conclusions of previous studies.[4]

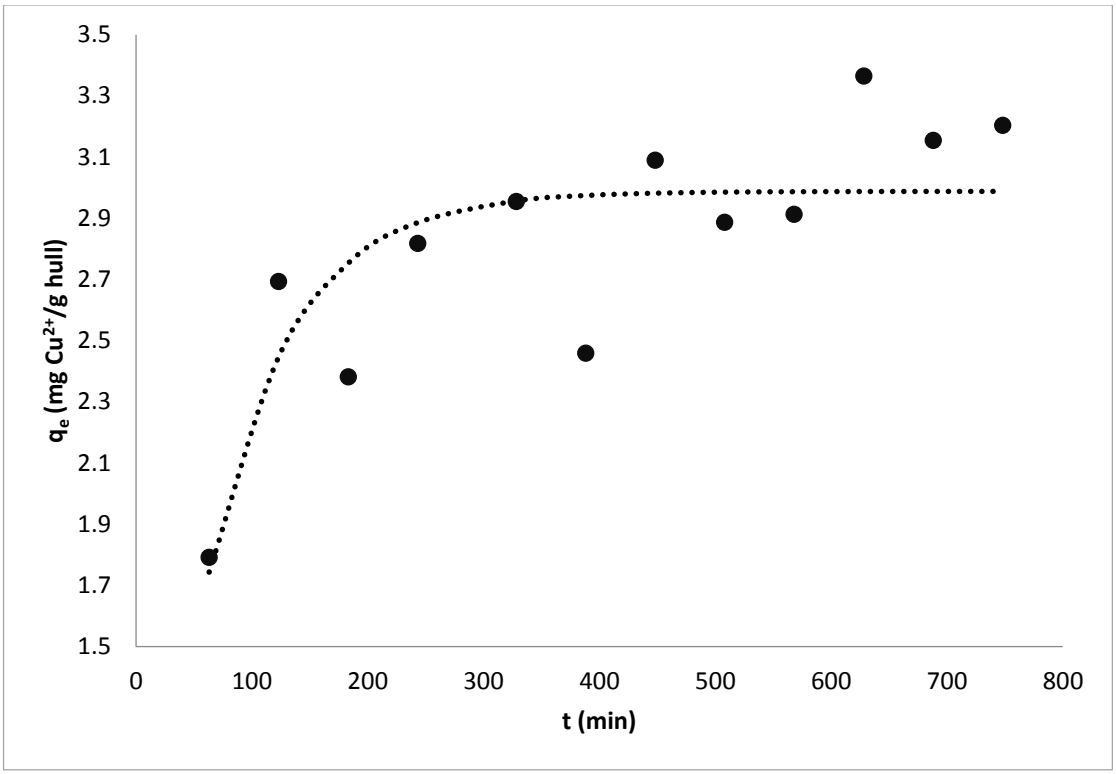


*Figure 5. Adsorption of $Cu^{2+}$ to unmodified peanut hulls over 12 hours for a 1000 ppm solution. The dotted line is the fit to Equation 8 with D =2.99±0.09 and B = 0.0134±0.003.*

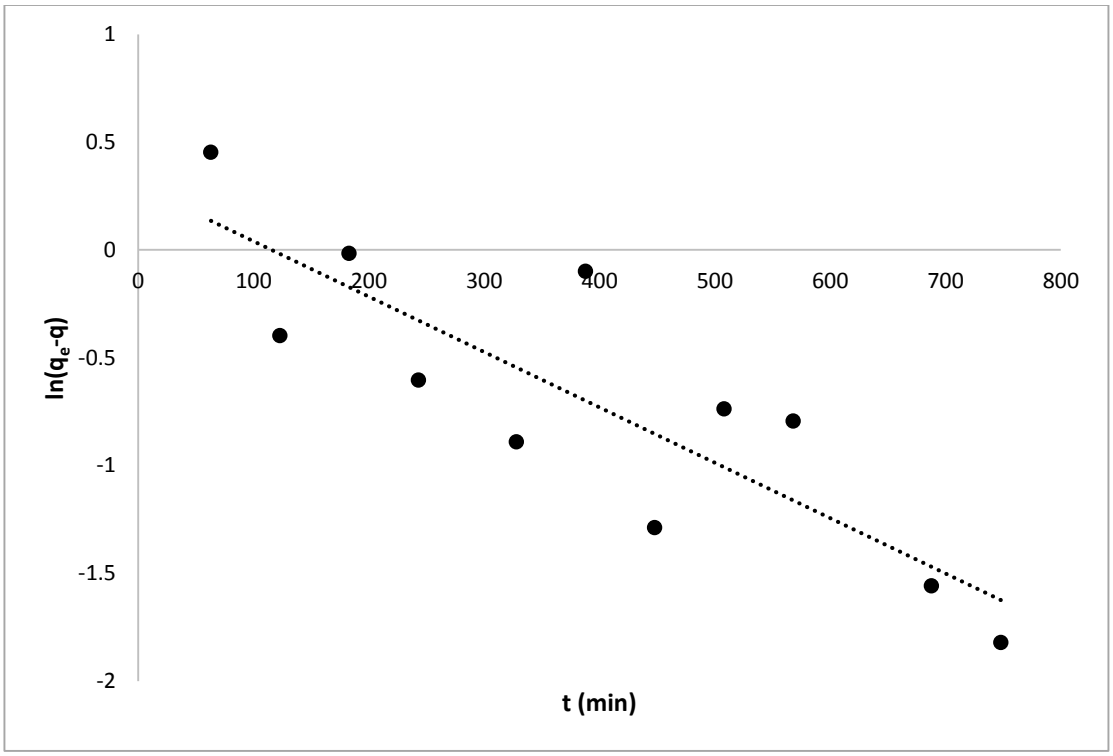


*Figure 6. Pseudo-first order kinetics model. The dotted line is the fit to Equation 14.*

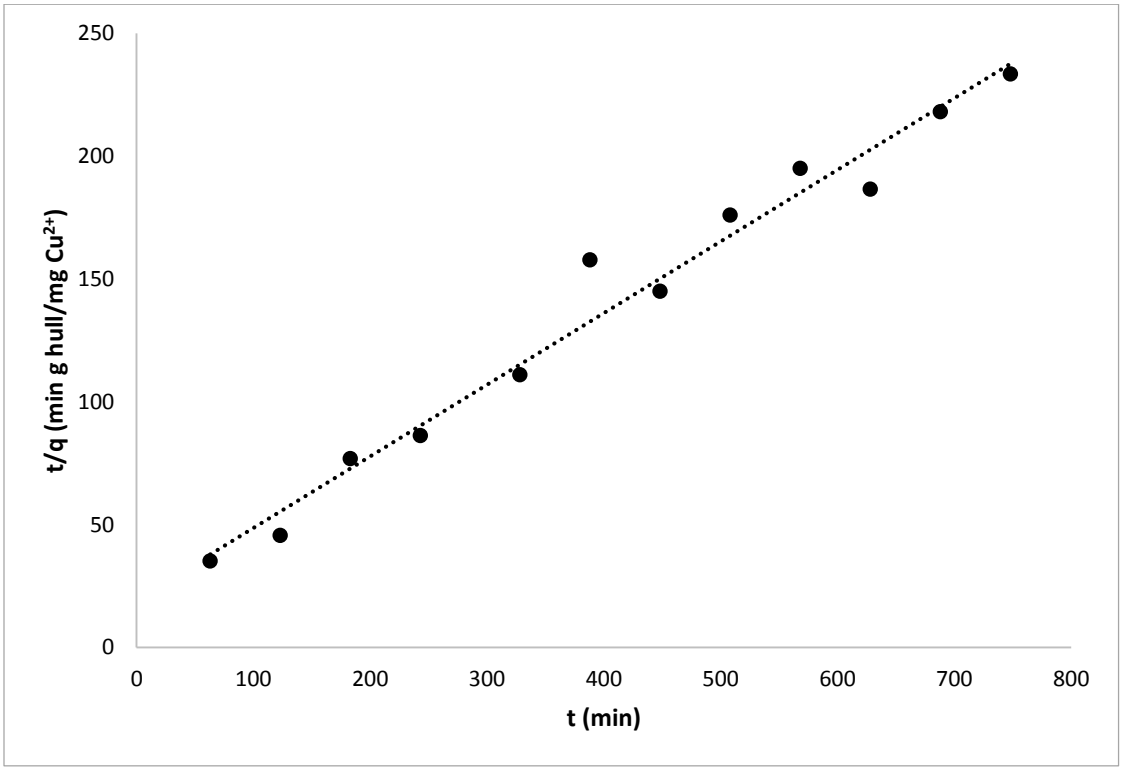


*Figure 7. Pseudo-second order kinetics model. The dotted line is the fit to Equation 15.*

*Table 2. Pseudo-first order and pseudo-second order kinetics fitting parameters.*

| Fitting Parameter | Pseudo-First Order | Pseudo-Second Order |
|---|---|---|
| $q_e$ | 1.3 mg $Cu^{2+}$/g hull | 3.4 mg $Cu^{2+}$/g hull |
| | ±1 | ±0.2 |
| $k$ | 0.0026 $min^{-1}$ | 0.0044 g hull/(mg $Cu^{2+}$ min) |
| | ±0.0005 | ±0.0002 |
| $R^2$ | 0.7267 | 0.9745 |

## CHEMICAL MODIFICATION OF HULLS

Figure 8 shows FT-IR spectra of modified and unmodified peanut hulls. A summary of peak assignments is in Table 3. For unmodified hulls, the band at 3316 $cm^{-1}$ corresponds to the OH stretching vibrational mode of the hydroxyl groups. The small peak at 1720 $cm^{-1}$ is assigned to the carbonyl stretching vibration of the carboxyl acid group in lignin. The band from 1575 $cm^{-1}$ to 1680 $cm^{-1}$ is due to the absorption of the bending mode of water molecules adsorbed to the hulls. The peaks at 1414 $cm^{-1}$ and 1357 $cm^{-1}$ are due to $CH_2$ bending and OH bending, respectively. The peak at 1242 $cm^{-1}$ is due to the OH in-plane bending from cellulose. The sharp peak at 886 $cm^{-1}$ is from the glycosidic CH deformation with ring vibration contribution and OH bending, characteristic of β-glycosidic bonds between glucose monomers in cellulose.[4,28] A detailed view of the peaks observed in the region of 650 $cm^{-1}$ to 1900 $cm^{-1}$ can be seen in Figure 9.

Differences between the IR spectra of the modified and unmodified hulls are evidence of a chemical modification. The bands above 2100 $cm^{-1}$ are largely unchanged. The most significant change is the disappearance of the peak at 1720 $cm^{-1}$ assigned to the lignin carbonyl, indicating that delignification occurred during the alkaline oxidation

process. Pure cellulose, the other major component of peanut hulls, does not have a carbonyl peak at 1720 $cm^{-1}$ as seen in Figure 10. A new peak corresponding to newly-formed carboxylate groups in cellulose was expected, since oxidation of alcohol groups in base would result in the formation of $COO^-$ groups. This peak is usually observed between 1650 $cm^{-1}$ and 1550 $cm^{-1}$.[29] However, a new peak in this region was not observed for modified peanut hulls. When pure cellulose was modified by the same procedure, there was also no significant change in the spectrum. Therefore oxidation cannot be confirmed, but it cannot be ruled out since the amount of C=O formed could be below the detection limit of the spectrometer. An estimation of absorbance from the quantity of C=O believed to be present in the hulls after modification is 0.013 (Appendix A). Peak-to-peak noise was approximately 0.002, so the peak should be small, but visible. However, a broad peak due to the bending mode of water molecules attached to the hulls appears from 1575-1680 $cm^{-1}$ which is the same region that a carboxylate stretching frequency should be. It is possible that any band due to carboxylate groups is overshadowed by the peak from the water bending mode.

Solid residue was obtained from the evaporation of the supernatant produced in the alkaline oxidation process. FT-IR was used to analyze this solid sample (Figure 11). The spectrum shows the carbonyl peak at 1747 $cm^{-1}$ that disappeared from the modified hulls spectrum. The spectrum of the solid residue also has peaks characteristic of aromatic components seen in the structure of lignin. The peak at 2957 $cm^{-1}$ is due to an aromatic C-H stretch. The peaks at 1567 $cm^{-1}$ and 1465 $cm^{-1}$ represent C=C ring stretching and the peak at 686 $cm^{-1}$ is due to the out-of-plane C=C bend.[29] This spectral profile shows that

lignin was solubilized by the alkaline peroxidation treatment and thereby removed from the hulls.

Commercial lignin was analyzed by FT-IR spectroscopy. The spectrum of the lignin was different from spectra reported elsewhere, showing no significantly similar peaks throughout (Figure 12).[28,30,31] The expected peaks representing aromatic stretches and vibrations were not present; neither were there peaks characteristic of carbonyls. The differences could be attributed to the manufacturer's isolation and purification process, which chemically modifies the lignin. The particular removal process was not specified by the company from which the lignin was purchased. The spectrum contains sulfonate peaks at 1355 $cm^{-1}$, 1193 $cm^{-1}$, and 1029 $cm^{-1}$, which suggests that the process involves a form of sulfur which ultimately binds and changes the structure of lignin. The spectrum confirmed that this commercial lignin is structurally different from the lignin of the peanut hulls, which may account for any differences when comparing their reactivity in this study.

*Table 3. Peak Assignments for FT-IR Spectra.*

| Peaks ($cm^{-1}$) | Assignment |
|---|---|
| Hulls/Cellulose | |
| 3600-3000 | OH stretch |
| 1720 | C=O stretch (unmodified hulls only) |
| 1575-1680 | water bend |
| 1424-1414 | $CH_2$ bend |
| 1361-1357 | ROH bend |
| 1242 | ROH in-plane bend (hulls only) |
| 886-895 | β-glycosidic CH deformation, OH bend |
| Solid Residue | |
| 1747 | C=O stretch |
| 2957 | aromatic CH stretch |
| 1567,1465 | C=C ring stretch |
| 686 | out-of-plane C=C bend |
| Commercial Lignin | |
| 1355 | asymmetric $S(=O)_2$ stretch |
| 1193 | symmetric $S(=O)_2$ stretch |
| 1029 | S-O-C stretch |

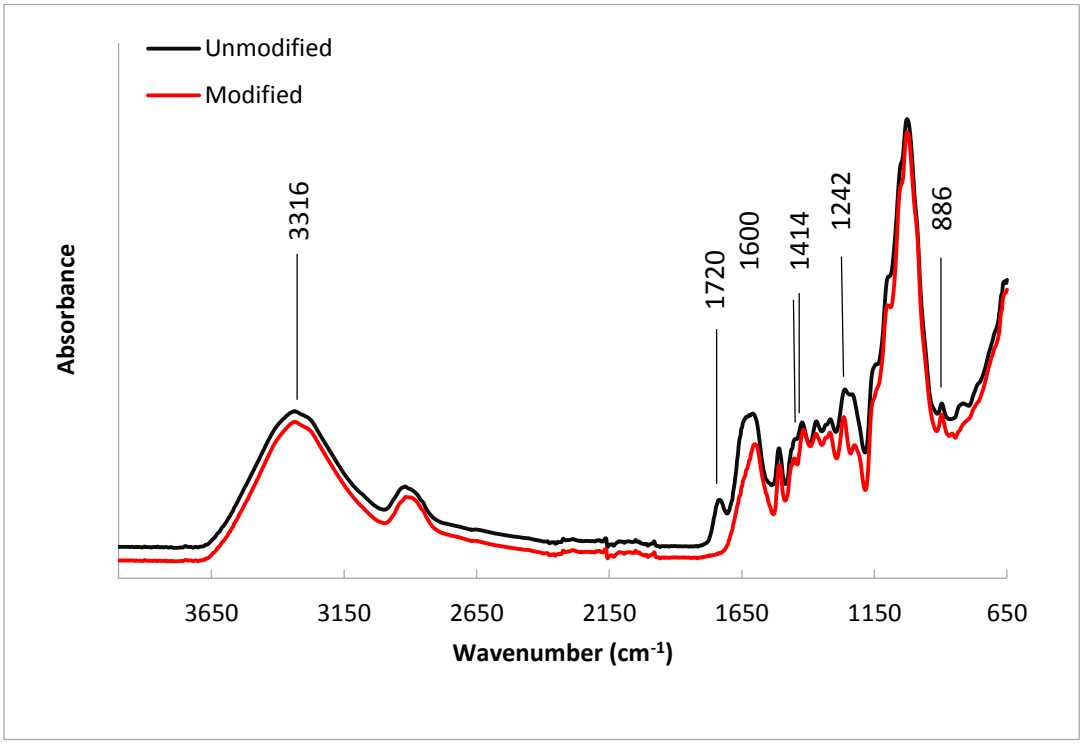


*Figure 8. FT-IR spectra of modified and unmodified peanut hulls.*

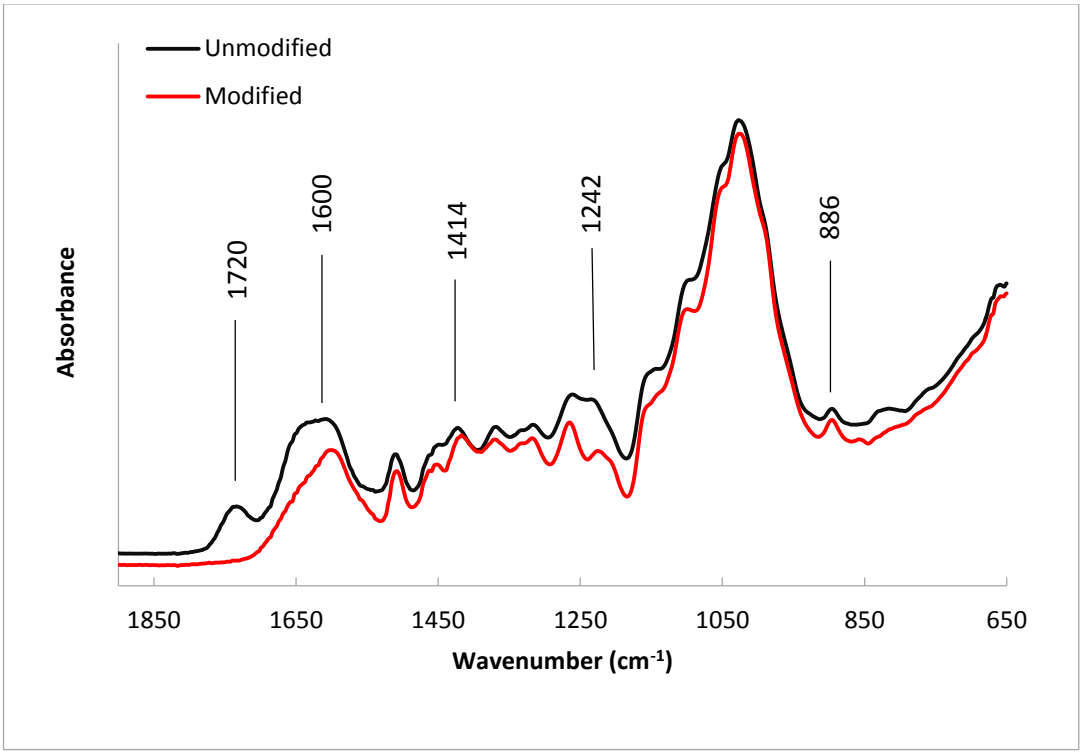


*Figure 9. Fingerprint region of the FT-IR spectra of unmodified and modified peanut hulls.*

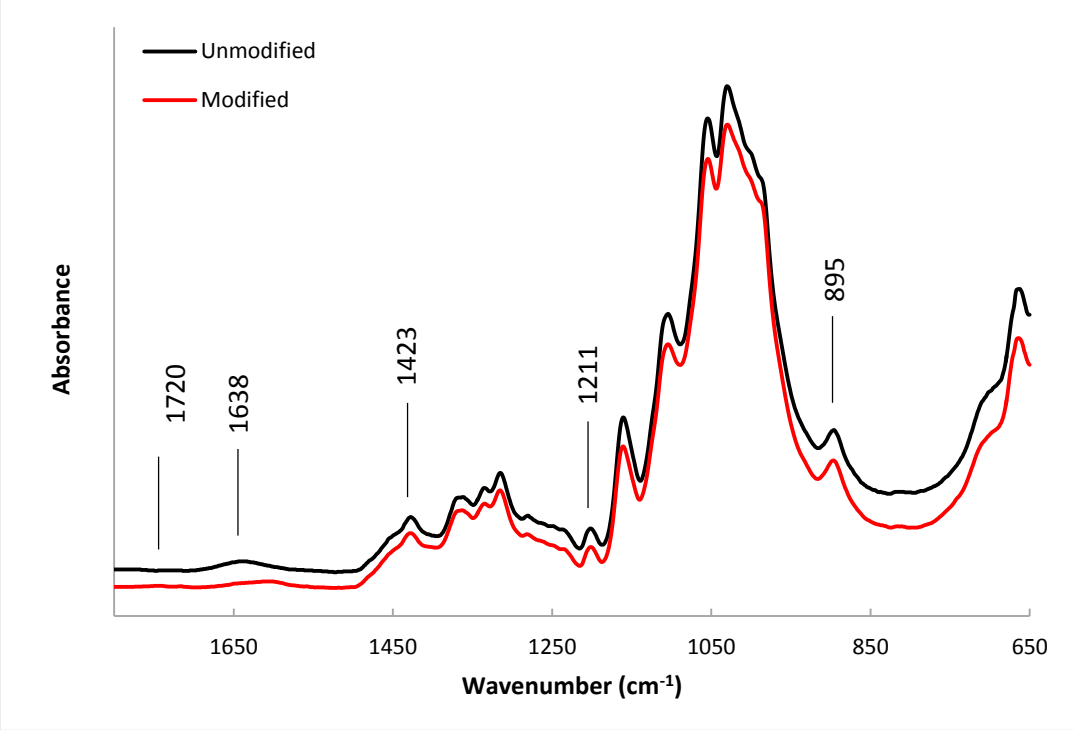


*Figure 10. FT-IR spectra of modified and unmodified cellulose.*

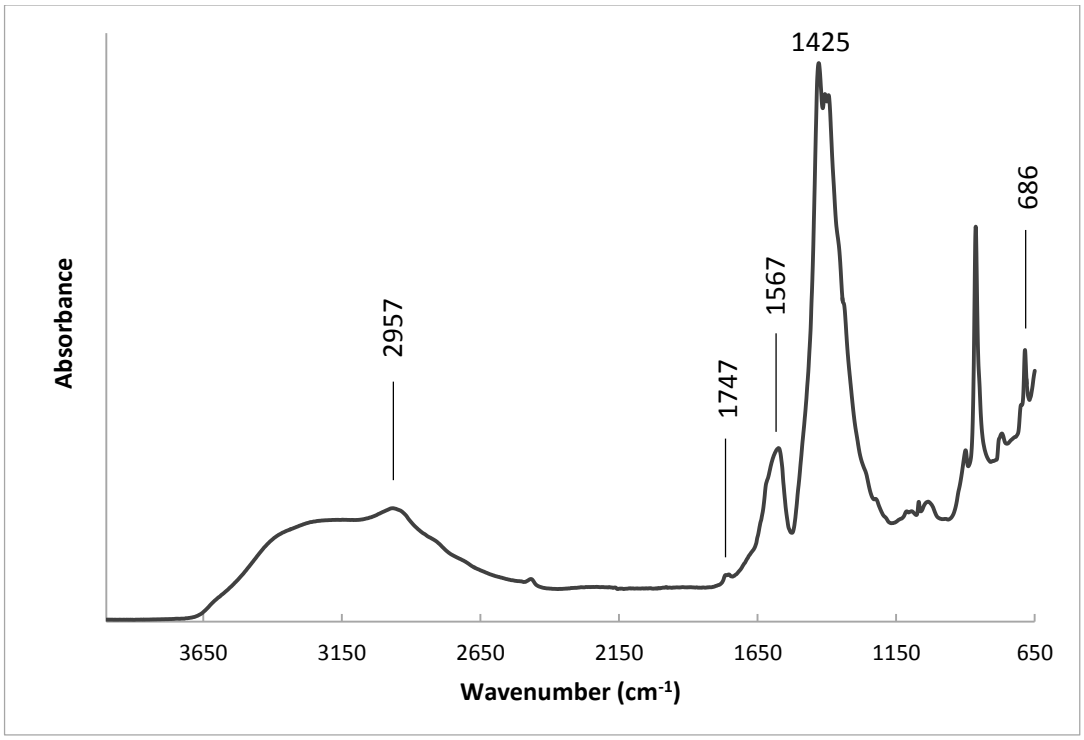


*Figure 11. FT-IR spectrum of residue isolated from the supernatant of the alkaline peroxide solution used in hull modification.*

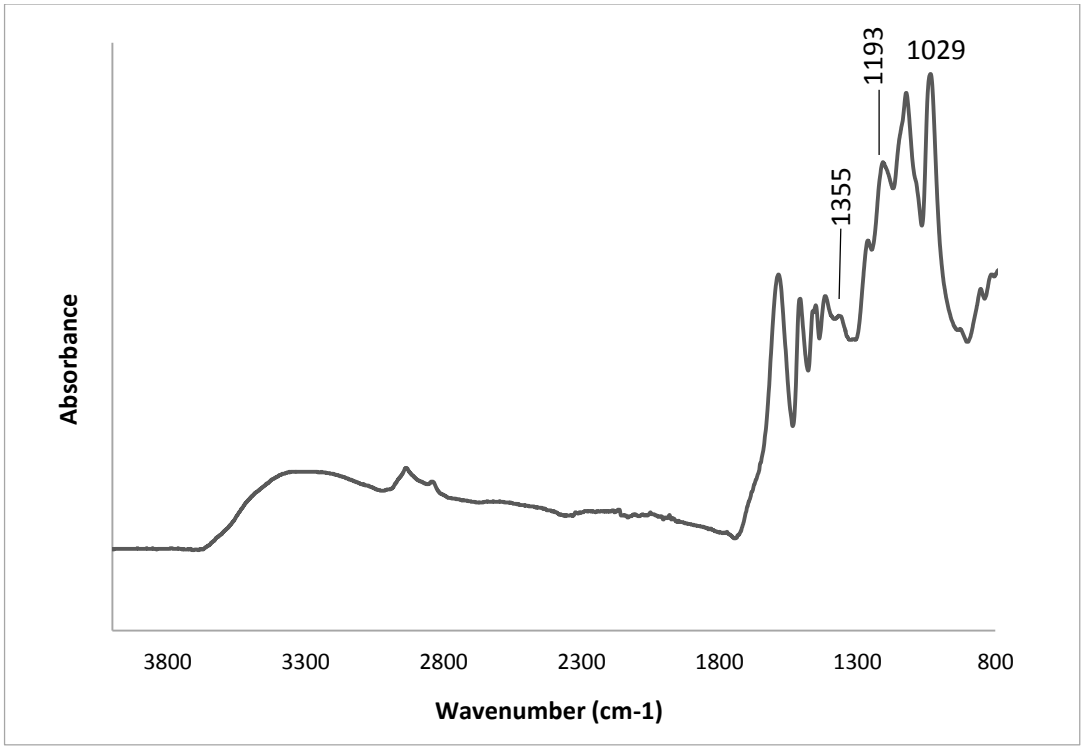


*Figure 12. FT-IR spectrum of commercial lignin with sulfonate peaks labeled.*

COPPER ADSORPTION

The adsorption data in Figure 13 show that the amount of $Cu^{2+}$ adsorbed per gram of hull ($q_e$) increases with an increase in equilibrium $Cu^{2+}$ concentration ($C_e$). There is a significant increase in surface coverage for the modified hulls compared to the unmodified hulls. The highest surface coverage measured for the modified hulls is 11 ± 1 mg $Cu^{2+}$/g of hull and for the unmodified hulls it is only 3.5 ± 0.6 mg $Cu^{2+}$/g of hull. The maximum capacities calculated from isotherm parameters for unmodified hulls in some previous studies are 13.34 ± 0.03 mg $Cu^{2+}$/g hull[10] and 17.99 mg $Cu^{2+}$/g hull.[4] The results in this study are low compared to previous studies. The difference may be due to differences in hull particle size because as particle size decreases, the surface area to mass ratio increases. Previous studies used hulls between 0.7 and 1 mm in size whereas the average hull size in this study was 1.33 ± 0.04 mm. The smaller surface area of the hulls in this study would diminish the maximum possible surface coverage. Also, sample shaking in the present study was conducted at 8 rpm, while in other studies, the solutions were shaken at 120 rpm.[4,10] The slower rate could result in fewer binding sites to be reached by the copper ions.

As expected, adsorption to the modified hulls is stronger due to the delignification. The removal of lignin makes the hulls more porous, which increases the surface area and the number of accessible binding sites. If the cellulose was oxidized, this may also cause an increase in the opportunity for metal ion chelation with carboxylate groups.[17,32]

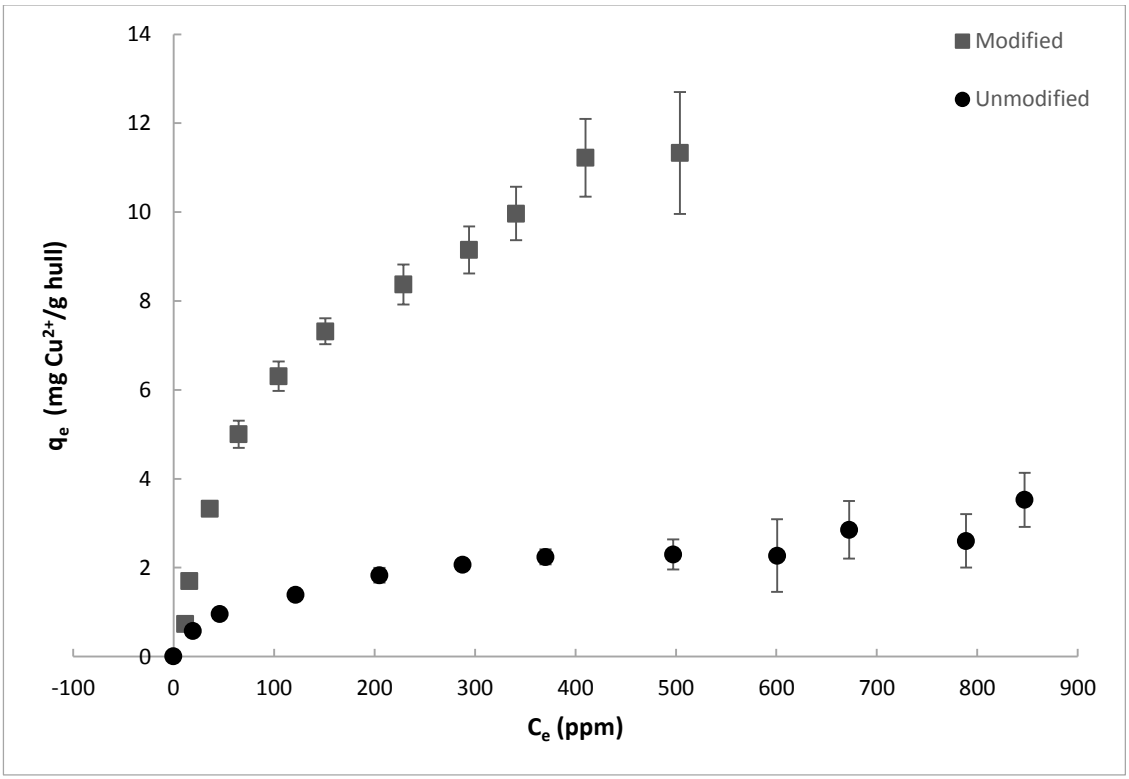


*Figure 13. Adsorption isotherm of $Cu^{2+}$ on unmodified and modified peanut hulls. Error bars represent uncertainty calculated by propagation of error.*

The adsorption process was completed on modified and unmodified cellulose to determine if the change in surface coverage was actually due to the cellulose and delignification as theorized. Figure 14 shows the adsorption data for modified and unmodified cellulose. There is an increase in surface coverage for the modified cellulose, while the unmodified cellulose shows almost no surface coverage. Since pure cellulose does not contain any lignin to be removed by the modification procedure, the increase in coverage cannot be attributed to an increase in surface area. Rather, a chemical modification (likely oxidation of alcohol groups to carboxylate groups) is responsible for the increase in binding sites.

Pure cellulose does not have a sufficient number of functional groups to efficiently adsorb metal ions from solution, therefore, minimal adsorption is observed.[21] The

adsorption observed in unmodified hulls is therefore likely to be due to the carbonyl functional groups in he lignin only. However, adsorption is low in this case because there are not a lot of carbonyls in the lignin and the sites may be blocked by cellulose. Adsorption of Cu(II) to pure lignin could not be determined because the commercially available alkaline lignin is soluble in the aqueous copper solutions and the alkaline peroxide.

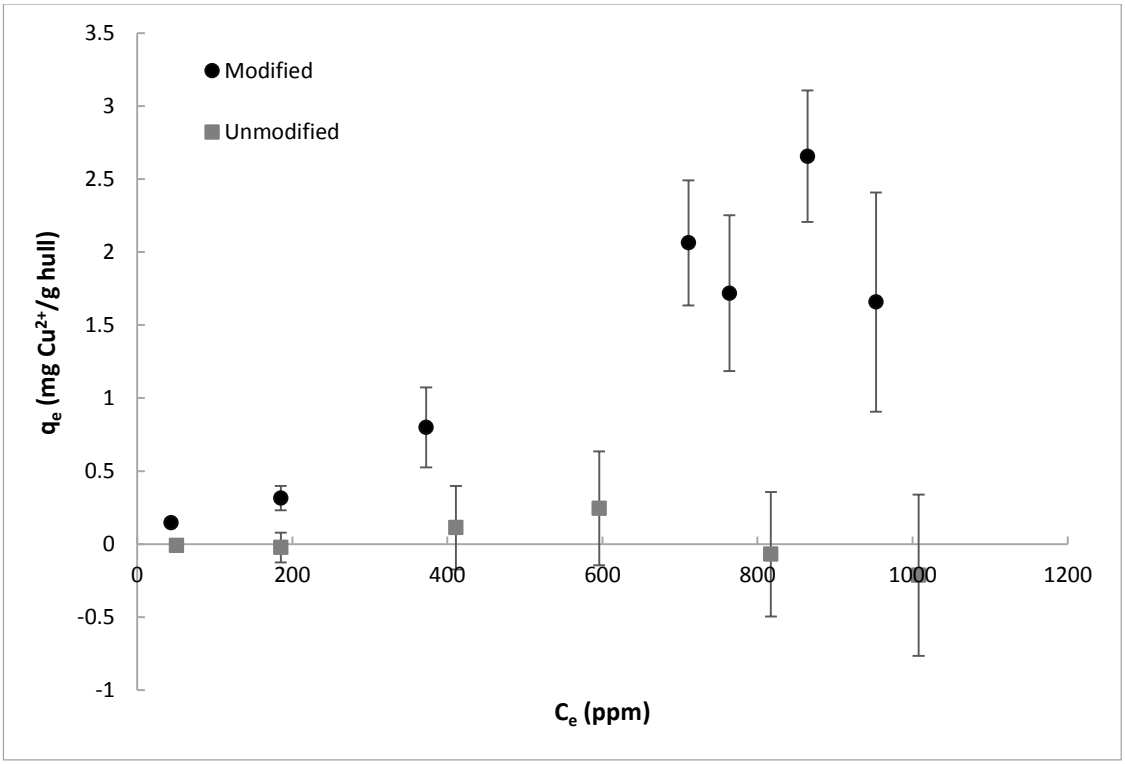


*Figure 14. Adsorption isotherm of $Cu^{2+}$ on unmodified and modified cellulose. Error bars represent uncertainty calculated by propagation of error.*

Several isotherm models were used for analysis of the biosorption process, but only the two models that best fit the study's adsorption data (Figure 13) are discussed. To determine which models fit better, the correlation constant, $R^2$, from the plots of each isotherm were compared. The two best-fitting models were the Langmuir[22] and Redlich-Peterson[25] models. Other models analyzed but not discussed include the Freundlich,[22]

Dubinin-Radushkevich,[22] Temkin,[33] Flory-Huggins,[34] Hill,[35] Hill-de Boer,[33] Sips,[36] and others.

Adsorption data fit to the Langmuir equation (Equation 3) is shown in a plot of $1/q_e$ versus $1/C_e$ (Figure 15). The fitting parameters are shown in Table 4. The calculated maximum surface coverage capacity ($Q_o$) is 2.7 ± 0.2 mg $Cu^{2+}$/g hull for the unmodified hulls and 28.3 ± 0.7 mg $Cu^{2+}$/g hull for the modified hulls. For the unmodified hulls, this calculated value is slightly lower than the observed maximum of 3.5 ± 0.6 mg $Cu^{2+}$/g hull. For the modified hulls, the calculated $Q_o$ is about 2.5 times higher than the observed maximum of 11 ± 1 mg $Cu^{2+}$/g hull. It is possible that a higher surface coverage could've been observed if measurements were extended to higher values of $C_e$.

$R_L$ is the adsorption intensity of copper ions on the hulls and can be calculated for every value of $C_e$. If $R_L$ is between 0 and 1, adsorption is favorable and if $R_L$ is greater than 1, adsorption is unfavorable. The $R_L$ values for the entire concentration range of the unmodified hulls fall between 0.065 ± 0.006 and 0.59 ± 0.05, showing an increase in favorable adsorption with increasing $C_e$. Over the entire concentration range of the modified hulls, $R_L$ values fall between 0.26 ± 0.02 and 0.88 ± 0.03, showing increasing favorable adsorption but with in an increased favorability relative to unmodified hulls.

The binding constant, *b*, also relates to the intensity of adsorption and is used to calculate $\Delta G_{ads}$ using Equation 5. If $\Delta G_{ads}$ is less than 8 kJ/mol, the adsorption process is said to be physisorption, and if it is greater than or equal to 8 kJ/mol, the process is chemisorption. For the unmodified hulls, $\Delta G_{ads}$ is 10.5 ± 0.9 kJ/mol, and for the modified hulls it is 14.5 ± 0.4 kJ/mol. Both energies are greater than 8 kJ/mol, therefore both processes are characterized as chemisorption.[4] The $\Delta G_{ads}$ is greater for the modified

hulls, showing there is more chemical ion exchange occurring on the surface than on the surface of the unmodified hulls. Overall, the modified hull data fit the Langmuir model well ($R^2$ = 0.9990), which suggests the biosorption process is homogenous, monolayer adsorption, with no interaction between adsorbed ions. Previous studies have concluded that the Langmuir model describes the biosorption process and that it is chemisorption.[4,10]

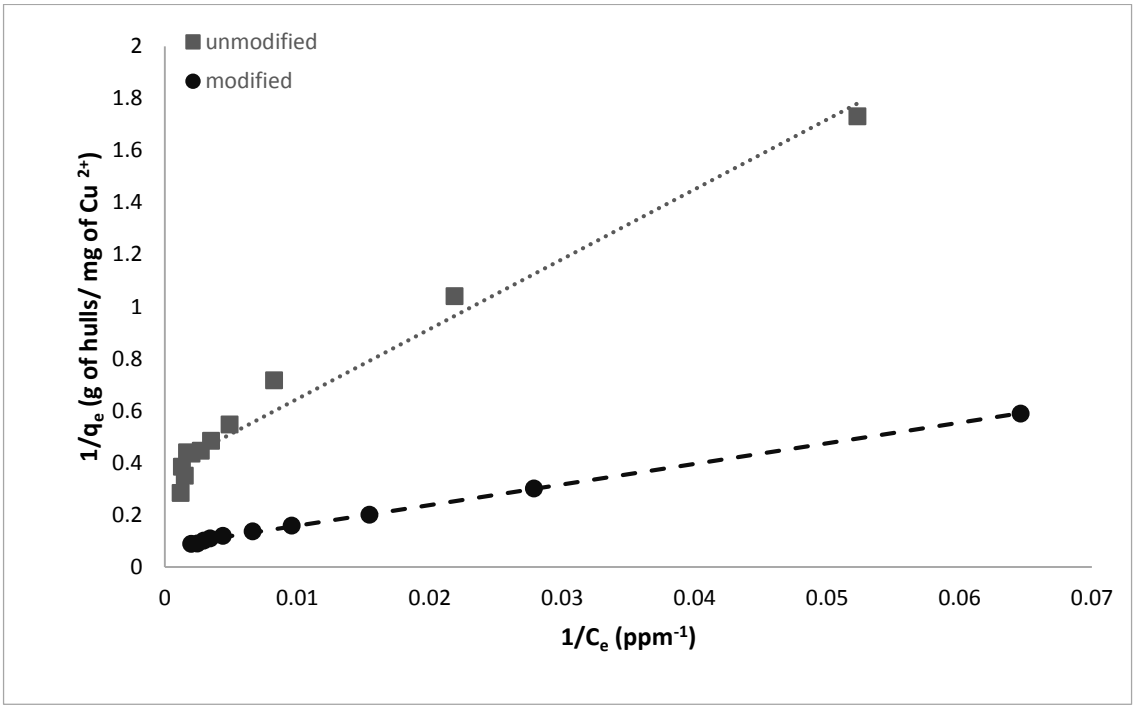


*Figure 15. Langmuir fit of the adsorption data to Equation 3.*

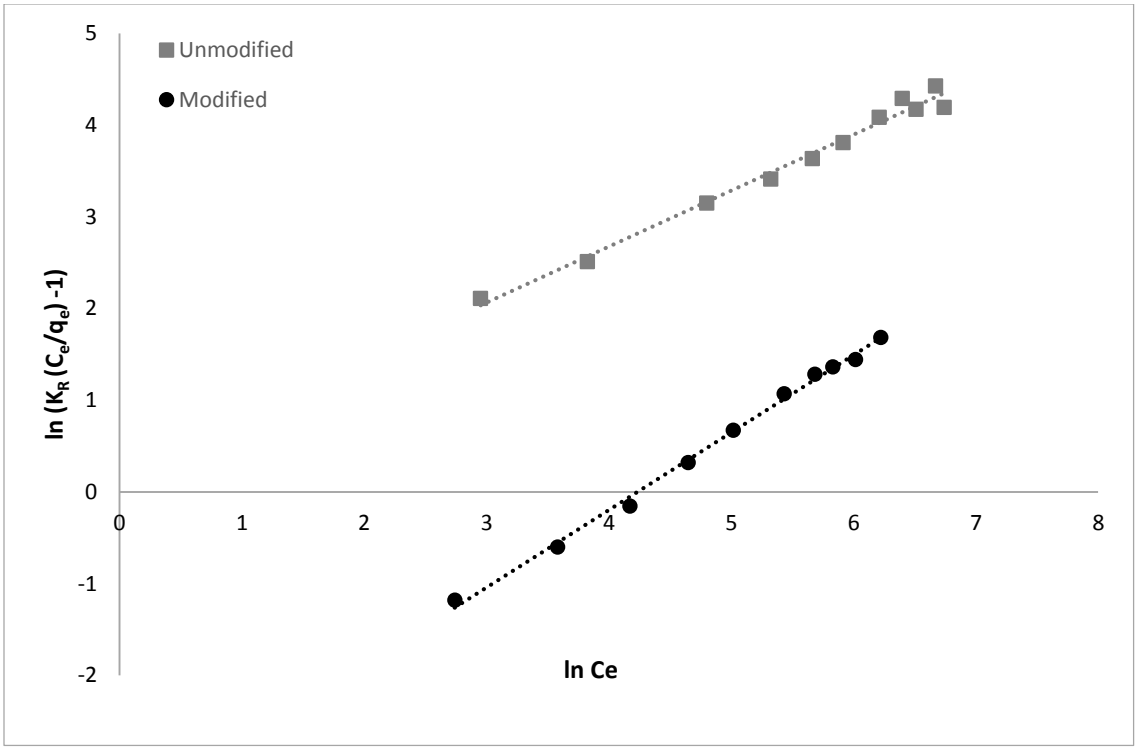


*Figure 16. Redlich-Peterson fit of the adsorption data to Equation 7.*

*Table 4. Langmuir and Redlich-Peterson isotherm parameters. (T=296 K)*

| Langmuir | Unmodified Hulls | Modified Hulls |
|---|---|---|
| $Q_o$ (mg $Cu^{2+}$/g hull) | 2.7 ± 0.2 | 28.3 ± 0.7 |
| $b$ (L/mg) | 0.014 ± 0.01 | 0.00280 ± 0.00008 |
| $\Delta G_{ads}$ (kJ/mol) | 10.5 ± 0.9 | 14.5 ± 0.4 |
| $R_L$ (min to max) | 0.065 ± 0.006 to 0.59 ± 0.05 | 0.26 ± 0.02 to 0.88 ± 0.03 |
| $R^2$ | 0.9746 | 0.9990 |
| **Redlich-Peterson** | | |
| $K_R$ (L/g) | 0.28 ± 1.97 | 0.14 ± 0.03 |
| $a_R$ (L/mg) | 1.2 ± 0.7 | 0.0308 ± 0.0008 |
| β | 0.62 ± 0.03 | 0.83 ± 0.02 |
| $R^2$ | 0.9851 | 0.9963 |

Given an $R^2$ value of 0.9746, the unmodified hulls do not fit the Langmuir model as well as the modified hulls. Consequently, the data was also fit to the Redlich-Peterson model, as shown in Figure 16, to see if incorporating some heterogeneity in the model improves the fit. The parameters are in Table 4. The Redlich-Peterson model describes both homogeneous and heterogeneous adsorption over a wide concentration range by combining the Langmuir and Freundlich equations with β summarizing the behavior. As β approaches 1, adsorption is better described by the Langmuir model and as β approaches 0, adsorption is better characterized by the Freundlich model. The Redlich-Peterson equation gives $\beta = 0.62 \pm 0.03$ for the unmodified hulls and $0.83 \pm 0.02$ for the modified hulls. Both values are intermediate between the Freundlich and Langmuir limits. The adsorption for the modified hulls, having a larger β, is better characterized by the Langmuir model than the unmodified hulls, which suggests increased homogeneous binding for the modified hulls. The modified hulls also fit the Redlich-Peterson model better than the unmodified hulls based on the correlation coefficients. This is in agreement with the results from Langmuir fitting, further confirming a more homogeneous, monolayer adsorption process. Although the modified hulls have a better fit for both Langmuir and Redlich-Peterson models, the unmodified hulls fit the Redlich-Peterson model better than the Langmuir model with an increased correlation coefficient of $R^2 = 0.9851$. This suggests that the adsorption of $Cu^{2+}$ on the unmodified hull surface may have some degree of heterogeneity that is not accounted for by the Langmuir model but is incorporated in the Redlich-Peterson model. Any heterogeneity in the unmodified hulls is likely removed by the oxidation/delignification process.

## ELECTRON MICROSCOPY

To further explore if adsorption was homogenous, as the isotherm models suggest, SEM images of hulls were acquired. EDX spectroscopy maps the copper on the surface of the hulls. The SEM image of an unmodified hull with adsorbed copper is shown in Figure 17. The lower panel of the figure shows the copper mapped on the surface (blue). The features in the SEM image can be seen in the mapped image, indicating that copper is evenly distributed across the surface at a magnification of 5000X. Figure 18 shows SEM images of a site of a modified hull with adsorbed copper and its copper mapped image. Curves have been placed in the images to point out similar features in each image. Figure 19, shows a different site on the same modified hull. Although the images reflect different hull textures and different chemical natures (modified and unmodified), all sites show homogenous adsorption of copper on the hull surface, which agrees with the isotherm models.

The copper mapping shows where the copper is on the surface but also gives the amount of copper on the surface. The average weight percentage of copper on the unmodified hulls is 1.6 % and for the modified hulls is 2.5 %. There is more copper present on the modified hulls than the unmodified hulls as seen in the adsorption isotherms. The adsorption data presented by SEM-EDX does show a smaller adsorption difference between the unmodified and modified hulls compared to the data of the isotherms. This difference may be attributed to the way the hulls were removed from the supernatant solution before use as samples in the SEM.

The unmodified and modified hulls were removed from the copper solution using vacuum filtration and then rinsed. To determine whether the adsorbed copper was

removed from the hulls during the rinse, an unmodified hull sample was rinsed with five aliquots of 5 mL of ultrapure water. The copper concentration of each aliquot was determined using ICP-OES. The concentration, *C*, of the solutions is shown in Figure 20. The amount of copper on the hulls decreased with each rinse and appears to level off. The copper removed from the hulls by the rinse may be residual precipitated copper from filtering the solution or bound copper. Further studies are needed to make such conclusion.

A possible experiment would be to perform an acid digestion of the rinsed hulls and analyze the copper concentration. If the amount of copper is equal to the amount of copper that was initially adsorbed, then precipitated copper was removed by the rinse. If the amount of copper is less than the amount of copper that was initially adsorbed, then bound copper was removed.

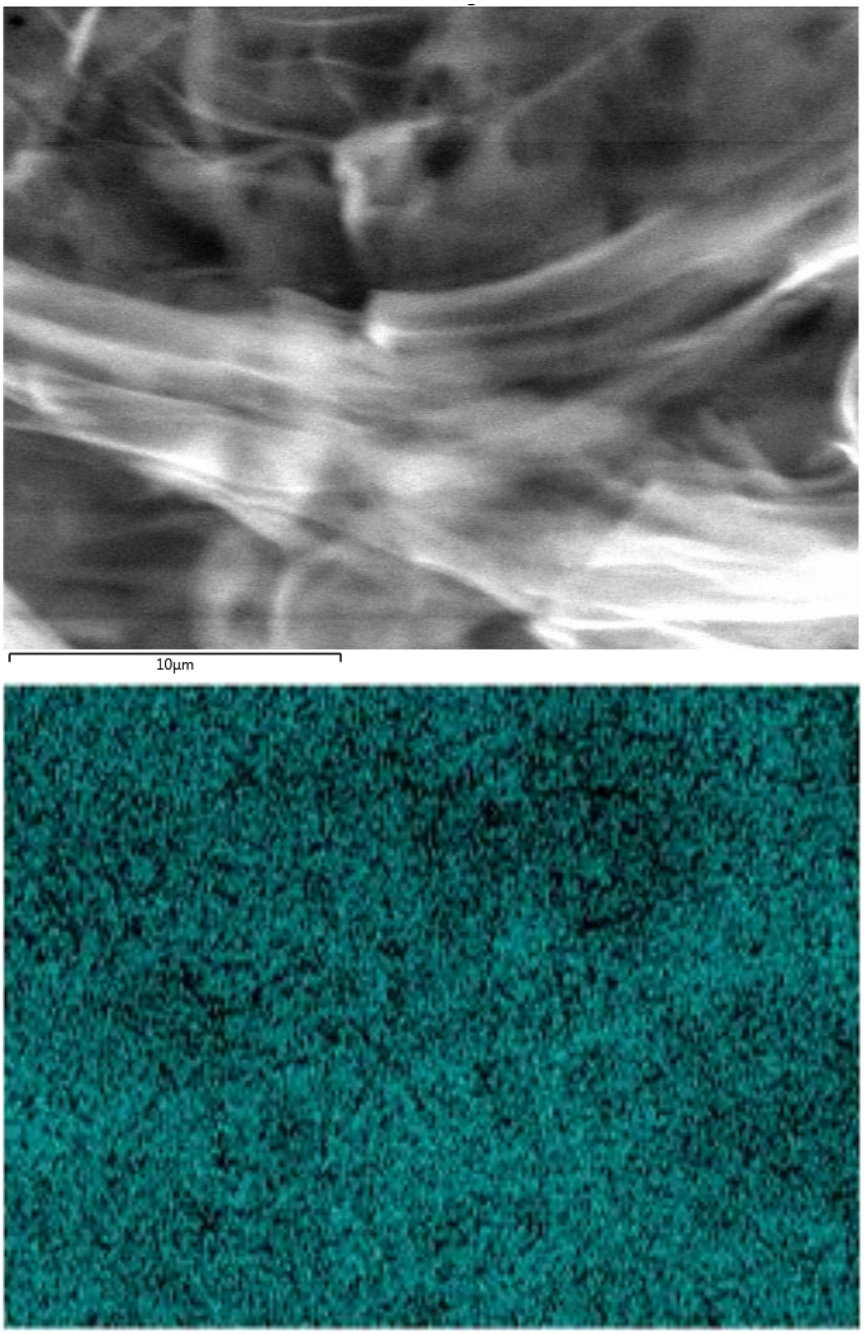


*Figure 17. SEM image of an unmodified hull (upper) with the copper mapped on the hull surface (lower).*

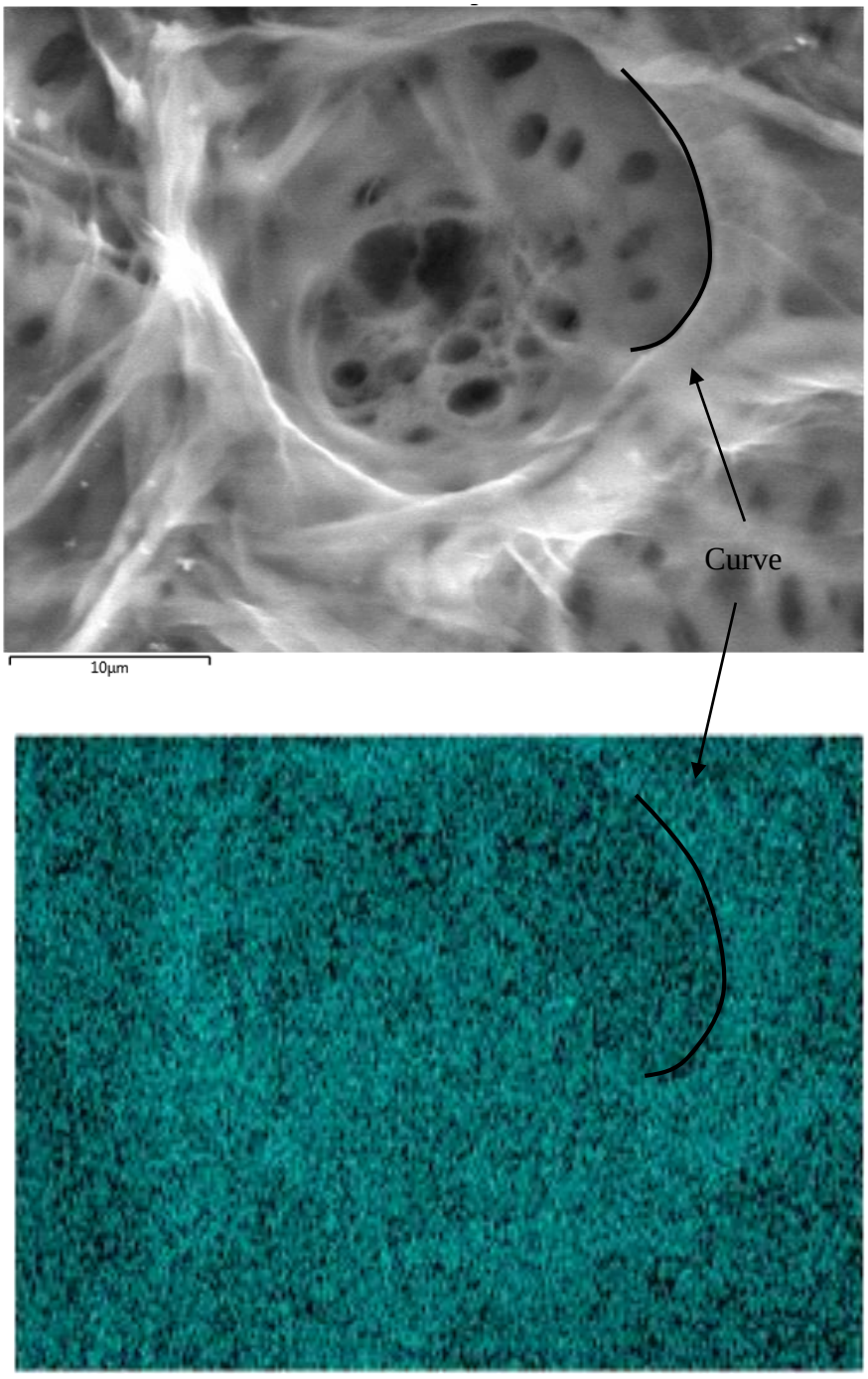


*Figure 18. SEM image of site A of a modified hull (upper) with the copper mapped on the hull surface (lower).*

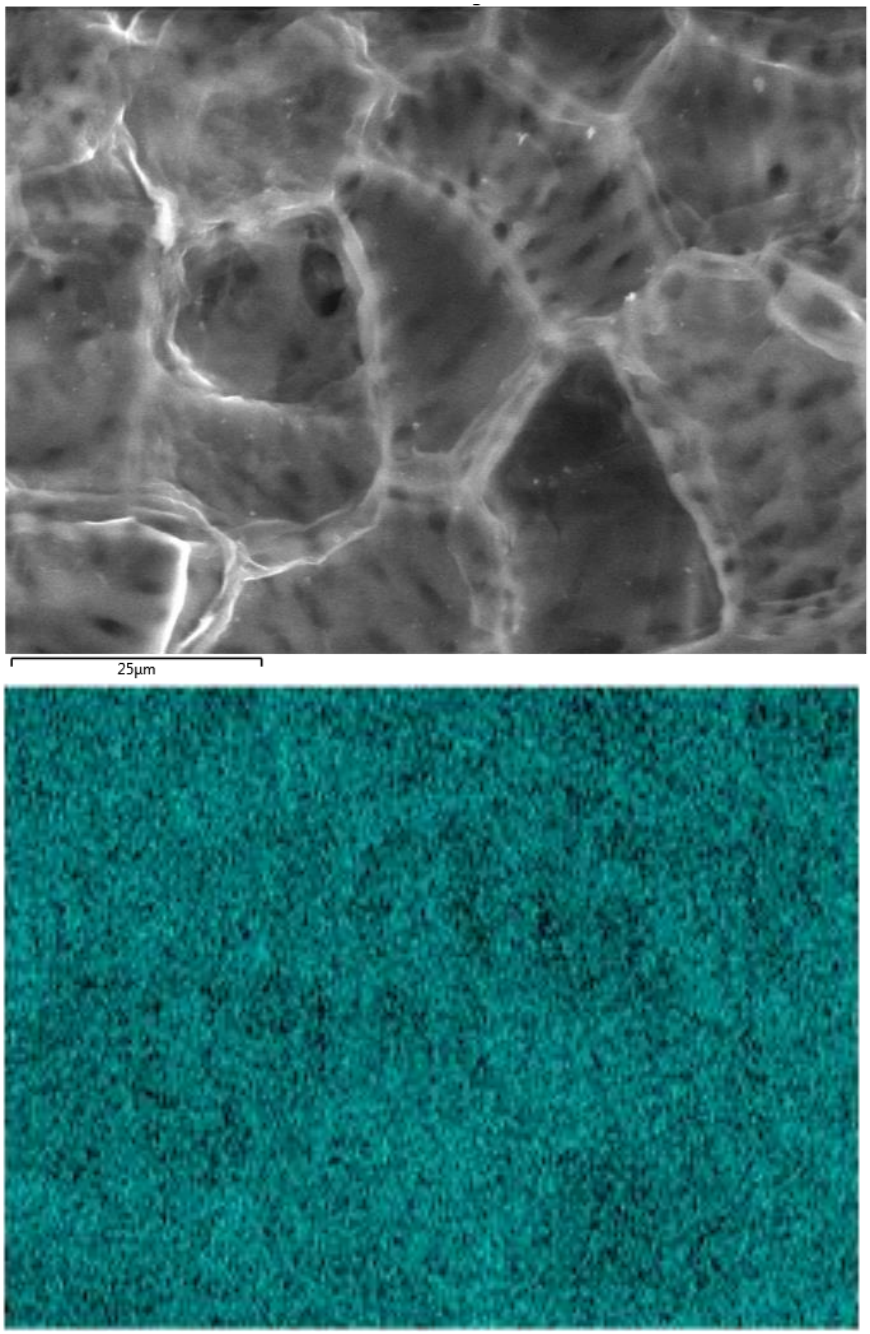


*Figure 19. SEM image of site B of a modified hull (upper) with the copper mapped on the hull surface (lower).*

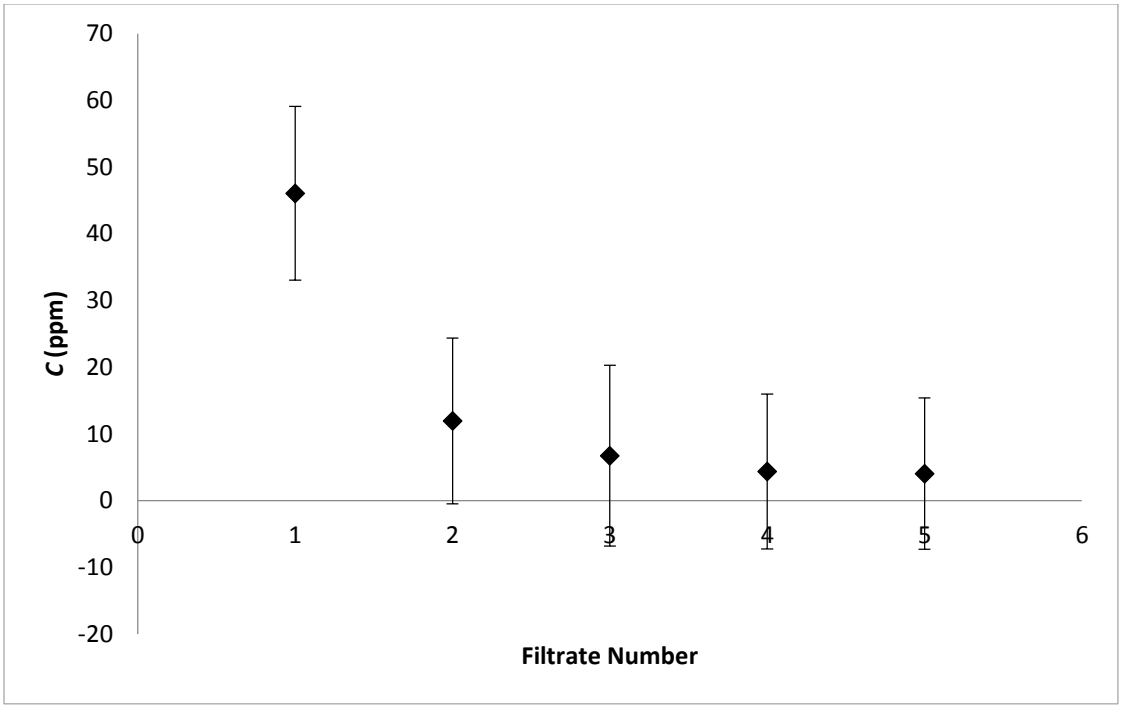


*Figure 20. $Cu^{2+}(aq)$ concentrations of the 5 mL aliquots collected in the supernatant when filtering the hulls from copper solution.*

# CHAPTER 4: CONCLUSION

Peanut hulls are effective at removing copper from aqueous solution through adsorption, making this process a candidate for wastewater treatment. The adsorption data indicated pseudo-second order kinetics and showed stronger adsorption with modified hulls than with unmodified hulls having maximum surface coverage of $11 \pm 1$ mg $Cu^{2+}$/g hull and $3.5 \pm 0.6$ mg $Cu^{2+}$/g hull, respectively. The modified hulls had undergone delignification as supported by FT-IR spectra and possibly oxidation of the cellulose. With the hulls rid of lignin, the newly formed carboxylate groups become available to the binding copper ions. The unmodified hull adsorption fit the Redlich-Peterson model better while the modified hulls adsorption data fit better to the Langmuir model. Both models describe homogenous adsorption, but the modified hulls have a more homogenous surface according to the higher β given by the Redlich-Peterson model. Free energy, $\Delta G_{ads}$, was calculated using $b$, giving $10.5 \pm 0.9$ kJ/mol for unmodified hulls and $14.5 \pm 0.4$ kJ/mol for modified hulls, confirming adsorption was favorable and fits a chemisorption model. Copper mapping of SEM images suggest homogeneous adsorption as well and shows the presence of more copper on the modified hulls than the unmodified hulls.

Through the present study, it is assumed the adsorption of aqueous copper using peanut hulls is a chemisorption, homogenous, and ion exchanging process involving the carbonyls on lignin in the unmodified hulls and newly formed carboxylate groups on cellulose in modified hulls. The increase in adsorption for modified hulls is also due to an increase in surface are from delignification. Although, SEM images give the amount of copper and where it is located on the surface, details of how the copper is physically

bound to the hull surface would provide insight and confirmation of the adsorption mechanism. X-ray photoelectron spectroscopy could provide this atomic scale information.

The current study has shown an affinity of peanut hulls to copper ions. Further research to see if peanut hulls have selective adsorption for other heavy metal ions, such as lead and cadmium, could expand the hull's potential as a biosorbent in wastewater treatment, and the best conditions for this process to run efficiently can be found.

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# APPENDIX A. ESTIMATION OF THE AMOUNT OF CARBONYL SAMPLED BY FT-IR SPECTROSCOPY

The concentration of carboxylate groups in a modified peanut hull sample could not be determined directly. Instead, the concentration was approximated using $Cu^{2+}$ surface coverage and several FT-IR instrument parameters. Attempts were made to overestimate the concentration as much as possible figuring that, if the calculated concentration was not measurable by FT-IR spectroscopy, then the actual concentration (less than the calculated value) would not be detectable.

The concentration of $COO^-$ sampled by the spectrometer (*c*) was approximated by assuming a 1:2 ratio of bound $Cu^{2+}$ ions to $COO^-$ surface groups. At the maximum surface coverage ($q_e$ = 11 mg $Cu^{2+}$/g hull for a solution initially containing 1000 ppm of $CuCl_2$), there would be 3.57 x $10^{-4}$ mol of $COO^-$/g hull. The beam path for the spectrometer samples a volume of 9.82 x $10^{-12}$ $m^3$. This volume (*V*) was calculated using a beam path radius[37] of 0.00125 m and a sample penetration depth[38] of 2 μm. The density (*d*) of peanut hulls was reported by Albrecht[12] to be 5-7 lbs/$ft^3$. Choosing a larger value for density provides a larger estimate of the carboxylate concentration, so 7 lbs/$ft^3$ or 112,129 g/$m^3$ was used for *d*. Using $d = m/V$, the mass of hulls sampled by the spectrometer (*m*) was determined to be 1.10 x $10^{-6}$ g. For this mass of hulls, there would be a maximum of 3.93 x $10^{-10}$ mol of $COO^-$ sampled by the spectrometer. Given the sample volume, this amount corresponds to a concentration of 0.040 M $COO^-$.

Beer's law relates absorption (*A*) to *c* and the substance's molar absorptivity ( $\varepsilon$ ):

$$A = \varepsilon lc$$

where *l* is the path length for the sample. The molar absorptivity for the carboxylate functional group has been reported for numerous compounds and ranges from 296-746 L $mol^{-1}$ $cm^{-1}$. The high value is for an average of 10 alkyl carboxylate salts in KBr pellets, reported by Flett.[39] Lower values are from similar salts in water[40] and methanol[41] solutions. If a large value of $\varepsilon$ is assumed for peanut hulls (say, 800 L $mol^{-1}$ $cm^{-1}$), then calculation of absorption using Beer's law will result in the largest possible value for *A*.

A value of twice the penetration depth can be used as an estimate for the path length in a single bounce attenuated total reflectance instrument. For this experiment, $l = 4$ μm. As described by Nishikida, this is not an entirely accurate representation, but for these purposes, the estimation will suffice.[42]

Given ε, *b*, and *c*, absorbance was calculated to be 0.013. Peak-to-peak noise was approximately 0.002, so the peak should be small, but visible. However, a peak due to hydrogen-bond stretching of water molecules attached to the hulls appears around 1680 $cm^{-1}$ which is the same region that a carboxylate stretching frequency should be. Given that there are likely many more water molecules in the hull than carboxylate groups, any band due to carboxylate groups is probably overshadowed by the hydrogen bonding stretching band.